The Effect of H_2S on Diamond Homoepitaxy

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The sulfur-doped diamonds possess a high potential for *n*-type semiconductive performance. We found that high-quality sulfur-doped homoepitaxial (001) diamonds grown by microwave plasma-assisted chemical vapor deposition (CVD) showed *n*-type semiconductive properties that are of potential practical use[1]. Horiuchi and co-workers reported that a sulfur-doped CVD homoepitaxial diamond layer realized a pn junction diode by a sequential growth of that on a boron-doped crystal grown by high-temperature, high-pressure synthesis[2]. Nebel and co-workers were succeeded in growing a sulfur-doped *n*-type homoepitaxial (001) diamond with a similar growth condition reported in Ref. 1; they revealed that the thermal ionization energy was in good agreement with the value reported in Ref.1[3]. These reported results indicate that sulfur offers great promise for producing *n*-type semiconductive diamonds. However, unresolved problems still remain in the CVD growth of high-quality sulfur-doped diamonds needed to obtain high-quality *n*-type semiconductive properties[4,5]. In this study, in order to gain an understanding of the effect of H_2S addition on the sulfur-doped diamond growth, we focused on the grown surface smoothness and the crystal quality varied with adding of H_2S. As diamond CVD growth proceeds on the surface, variations of the surface smoothness is expected to tell us how the growth is affected by the adding of H_2S in the gas phase. The variations also indicate differences in the crystal quality, as well.

The growth conditions for sulfur doping CVD experiments are summarized in Table 1. For the sulfur doping, we used hydrogen-diluted H_2S (purity; 6 N) as a dopant gas. High-pressure and high-temperature (HPHT) synthetic Ib diamond (001) crystals were used as substrates for the homoepitaxy. The roughness of the surfaces were different each other, for these surfaces were obtained by a mechanical polish. Before starting CVD growth, the substrates were kept in a hydrogen-plasma for 30 min. in order to prepare similar surfaces by hydrogen plasma etching[6].

The surface morphology of the homoepitaxial diamonds was observed by atomic force microscopy (AFM), which clarified the effect of adding H_2S to the surface smoothness. Addition of H2S in small amounts contributed to the suppression of the secondary nuclei formation and yielding a smoother surface. Cathode luminescence spectroscopy (CL) examined the crystal quality. The crystal quality had a closer relationship with the surface smoothness. Sharp Free-exciton (FE) peaks were observed from the sulfur-doped diamond which had a smoother surface.

For the electric measurements, the S-doped homoepitaxial diamonds were treated to make ohmic contacts[4]. Hall-effect measurements were performed by the van der Pauw method (Bio-Rad, HL5500 Hall system) within a temperature range of 250 - 550 K[4]. The detailed measurement conditions were done as written in Ref.4. The n-type semiconductive property was sensitive to the crystal quality. *N*-type conduction could be realized in high-quality, sulfur-incorporating (001) homoepitaxial diamonds.

In this presentation, the interaction of sulfur with diamond surfaces will be discussed for understanding the effect of H_2S addition on the crystal growth.

Table 1 Growth conditions

Reactant gas	CH_4(1.0 %)/H_2S/H_2
H2S conc.	0-1000 ppm
Total gas flow rate	500 ml min^{-1}
Total pressure	50 torr
MW power	800 W
Substrate temperature	650-825 °C
Substrate	HPHT-diamond (001)

References

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